QUARTERLY STATUS REPORT

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FABRICATION OF SYNTHETIC MICACEOUS MATERIALS

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A. Mica-Bonded Metal and Ceramics

The bonding program was discontinued in view of the re-application of the work primarily towards electrical requirements. Prior work in the exploration of cermets indicated that, for machining, the most desirable materials consisted of metal powder and phlogopite mixtures, as the cermets utilizing metal chips, wire, or wool, although capable of being sawed or milled, were destroyed by conventional machining techniques such as turning on the lathe, generally by dragging out the metallic strands. The phlogopite mixtures involving silicon carbide were extremely abrasive and could not be turned either by cutting tools or grinding wheels. Any further work in this direction, should it again become of interest, would be directed primarily toward the phlogopite bonding of oxides, carbides and nitrides chiefly for abrasive or refractory applications involving the development of a lower melting-machinable phlogopite bond to aid in the consolidation and fabrication of those ceramic bodies which are difficult to handle by conventional techniques. This field appears to have a great deal of potential and should be studied more intensely. The metal-ceramic mixtures, as discussed last month, are somewhat low in strength although appreciably stronger than mica itself. However, should machinable mica-metal combinations be of interest or potential usefulness, there appears to be no great problem, from the fabrication point of view, in producing these materials.

B. Mica Production

On scaling up the size of batches of mica (compact size) in the pilot plant, it was noticed that increasing amounts of magnesium fluoride were detected as an impurity in the mica. Although the presence of magnesium fluoride in fluor-phlogopite appeared advantageous from the standpoint of bonding metals and ceramics, it also appeared to contribute to mica contamination through reaction with dies and inserts as well as to spalling and dimensional changes where hot pressing large bodies of the fluor-phlogopite. Consequently, the factor of time was again evaluated in respect to the large batch ingredients which were more liable to contain MgF_2 to investigate means of reducing this impurity in order to produce on a larger scale the better-grade electrical micas.

The batch ingredients for producing the four types of mica were blended in stoichiometric ratio with a 5% excess of the fluorine donating compound and cold pressed at 5000 psi with subsequent firing at optimum temperatures previously determined with periods of time up to five hours. The samples were manually pulverized, screened through a 35 mesh Taylor screen, and analyzed petrographically for mica content by the Bureau of Mines Electrotechnical Laboratory at Norris, Tennessee. The results of these tests are shown in Table I.

TABLE I

TIME OF REACTION VS. COMPOSITION FOR SYNTHETIC FLUOR-PHLOGOPITE

Time	Temperature	Approximate Composition
a. Normal		
1 hr.	1050°C.	Mica - 50-60% Glass - 15-20% Quartz - 5-10% MgF_2 - 10-15%
2 hrs.	1050°C.	Mica - 60% Glass - 15-20% MgF_2 - 10% Quartz - 5%

TABLE I

(CONTINUED)

Time	Temperature	Approximate Composition
3 hrs.	1050°C.	Mica - 70-75% MgF_2 - 10% Glass - 10-15% Quartz - 2-3%
4 hrs.	1050°C.	Mica - 85-90% Glass - 2-3% MgF_2 - 10% Quartz - trace
5 hrs.	1050°C.	Mica - 95% MgF_2 - 2-3% Glass - < 2% Quartz - none
b. Boron		
1 hr.	975°C.	Mica - 50-70% Glass - 30-50% MgF_2 - < 5%
2 hrs.	975°C.	Mica - 70-80% Glass - 20-30% MgF_2 - < 2%
3 hrs.	975°C.	Mica - < 95% MgF_2 - < 2% Glass - trace Forsterite - trace
4 hrs.	975°C.	Mica - < 98% MgF_2 - trace Forsterite - trace
5 hrs.	975°C.	Mica - > 95% Forsterite - < 4% Glass and MgO - 1.0%
c. Barium-Lithium		
1 hr.	1050°C.	Mica - 90% Glass - < 5% MgF_2 - 3% BaF_2 and $BaSiO_3$ - < 2%
2 hrs.	1050°C.	Mica - 95% Glass - < 2% BaF_2 and $BaSiO_3$ - < 2%

TABLE I

(CONTINUED)

Time	Temperature	Approximate Composition
3 hrs.	1050°C.	Mica - > 98% BaF_2 + $BaSiO_3$ - trace Dark inclusions - < 1%
4 hrs.	1050°C.	Mica - > 95% Dark inclusions - 3% Fluorides and others - trace
5 hrs.	1050°C.	Mica - > 95% Forsterite - 1.0% Glass - 1-2%
d. Barium		
1 hr.	1050°C.	Mica - 70-80% Glass - 10% MgF_2 - < 5% BaF_2 + $BaSiO_3$ - 10-25%
2 hrs.	1050°C.	Mica - 80-90% Glass - 5% Fluorides - < 5% $BaSiO_3$ + inclusions - 3%
3 hrs.	1050°C.	Same as 2 hrs.
4 hrs.	1050°C.	" " " "
5 hrs.	1050°C.	" " " "

From this data it can be seen that the boron and barium-lithium mica were the most reactive, forming in less than three hours. Of the four types of mica, the boron and barium-lithium varieties showed a tendency to lose sufficient fluorine to cause formation of forsterite in five hours. Normally, forsterite is the major impurity found in mica rather than the fluorides which have been showing up in the low temperature reaction process used at the Brush Beryllium Company pilot plant.

To determine the effect of the diameter of the compact vs. the reaction efficiency, the dried batch ingredients for normal phlogopite mica

were blended in a stoichiometric ratio using a 5% excess of K_2SiF_6. The reactants were compacted at room temperature and 2500 psi in various diameter molds, maintaining the diameter-length ratio of 0.75. The compacts were fired for five hours after reaching a temperature of 1050°C., with results as shown in Table II.

TABLE II

SURFACE AREA EXPOSED VS. REACTION EFFICIENCY OF NORMAL MICA

Compact Diameter	Compact Height	Surface Area per lb. $in.^2/lb.$	Approximate Composition
1-1/2"	1.14"	96	Mica - 85% MgF_2 - 5% Cristobalite - 0%
2-1/4"	1.46"	73	Mica - 85% Glass - <5% MgF_2 - <5% Quartz - <3%
3-1/2"	2.34"	40	Mica - 80% MgF_2 - 15% Glass - 5%
4-1/2"	3.15"	32.9	Mica - 70% Glass - 10-15% MgF_2 - 20%
6.0"	4.77"	22.2	Mica - 70-75% Glass - 15-20% MgF_2 - 10%
8-3/4"	6.1"	17.4	Mica - 65% MgF_2 - 25% Glass - 5%

The mica content progressively decreased with increases in diameter of the compact. One supposition might be that of the excess of fluorine in the form of K_2SiF_6 which may be causing the reaction of SiF_4, a decomposition product of K_2SiF_6 to form magnesium fluoride by fluorination of MgF_2. In the larger compacts, there is less chance for the decomposition product SiF_4 to escape; consequently, a much greater amount of magnesium fluoride may be

formed. It is also suspected that in handling large lots through tumbling, the mixture is insufficiently mixed and the SiF_4 formed will be largely utilized in attacking the magnesium oxide, rather than as a combined reaction for the formation of fluor-phlogopite. It was, therefore, concluded that in order to make synthetic fluor-phlogopite with large compacts by the low temperature solid phase method, the times and temperatures which have been established for small lots were satisfactory, but that very intimate blending and possibly reduction to K_2SiF_6 should be carried out. Poor blending as a cause of incomplete reaction was also indicated by the residual quartz in reaction runs.

In order to determine the effect of blending on the reaction, these experiments will be repeated next quarter, as far as the large reaction compacts are concerned, the blending to be performed in a newly installed twin shelled blender, thus attempting to eliminate the variables caused by inconsistencies in blending efficiency.

C. Hot Pressing

Stock blocks of boron and normal mica 4-1/2" in diameter by 6"-11" long are being hot pressed to a density of 2.7 g/cc. It was found that blocks consisting of a series of cold pressed compacts 4-1/2" in diameter by 3" high which were stacked in a lamellar fashion in the hot pressing die could be pressed as a single piece 10" long, but upon cutting the cylinder longitudinally along its diameter, it cracked in the direction transverse to the axis of the cylinder along the segment boundaries. Although this would indicate that the method is unsatisfactory for making large pieces, it does show that a considerable vertical depth can be hot pressed at one time, allowing the hot pressed compact to be broken along the segment boundaries. This is of importance in considering the economic potential of the process.

A boron mica block 8.9" in diameter and 11" long was also hot pressed in a similar fashion, as well as a block 12" in diameter and 7" long. Even though these large pieces were cooled for a long time (up to 36 hours in the die) sufficient thermal shock took place to cause severe spalling and cracking. Consequently, although equipment is available to produce 12" diameter pieces, pressings of this size should be limited to pieces no greater than 4" thick. For the present, 6" long pieces no greater than 4-1/2" in diameter will serve as stock blocks for the evaluation program until more information as to the largest minimum dimension which can be achieved, to prevent spalling due to thermal shock, is established.

D. Evaluation

During the last quarter samples were distributed to 21 manufacturers and government agencies for evaluation of a number of applications. The potential uses included the following:

1. Electrical and heat insulation.
2. Abrasive and abrasive wheel binder.
3. Filler in electrical plastics.
4. Corrosion resistant material at high temperatures.
5. Spacers for vacuum tubes.
6. Stainless steel cermet.
7. Printed circuit base.
8. Applicability as a block-talc substitute.
9. High temperature dielectric.
10. Dielectric under high temperature steam.
11. Refractory under thermal shock conditions.

In addition to these tests, a quantity of hot-pressed material was shipped to the Naval Research Laboratory in a co-operative effort to determine the applicability of normal fluor-phlogopite as tube spacer material which is

now considered the major objective of this program. This application was studied and a report* was made by Mr. T. E. Hanley of the Naval Research Laboratory. His major conclusions were as follows:

1. Hot pressed synthetic fluor-phlogopite pressed to 2.73 g/cc was vacuum tight maintaining a constant pressure of 2.2×10^{-9} mm. Hg after baking at 390°C. and 5×10^{-7} mm. after air baking at 800°C.

2. The material was machinable to 10 mil discs with an ordinary high speed cutoff tool and could be ground to 2.5 mils. However, attempts to punch holes in samples of 10 and 30 mils thickness were unsuccessful on the intial attempt.

3. Synthetic fluor-phlogopite could be brazed at 820°C. in vacuum with titanium core solder to copper to form a vacuum tight joint. Better wetting of the mica was obtained when titanium hydride was used in addition to the brazing material.

4. The material had less than .0002" in 1-1/2" diameter shrinkage when fired for one hour at 1100°.

5. A dielectric constant of 5.72 was determined at 9375 mc with a loss tangent less than 0.005 (tests at Brush Beryllium Co. on this material gave a loss tangent of 0.0014 at 1 mc).

6. The final conclusion of this report was that "synthetic fluor-phlogopite has good vacuum properties, is readily machinable to exact size, is brazable and of low loss".

E. Plans for Future Work

During the next quarter, the following project aims will be considered:

1. Examine the effect of blending, effect of excess fluoride, and time and temperature of resistance on the electrical properties of synthetic fluor-phlogopite after hot pressing.

*T.E. Hanley, "Synthetic Mica for Vacuum Tube Use", Presented at Tube Techniques Conference, N.Y., N.Y. October 14, 1953

2. The production of a quantity of 4-1/2" x 10" stock blocks for continued evaluation of hot pressed mica.

3. Additional samples will be furnished to the Naval Research Laboratory for evaluation of the use of synthetic fluor-phlogopite as tube spacer material.